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Laboratory Technique for Measurement of pH for Corrosion Control and Water Not in Equilibrium with the Atmosphere

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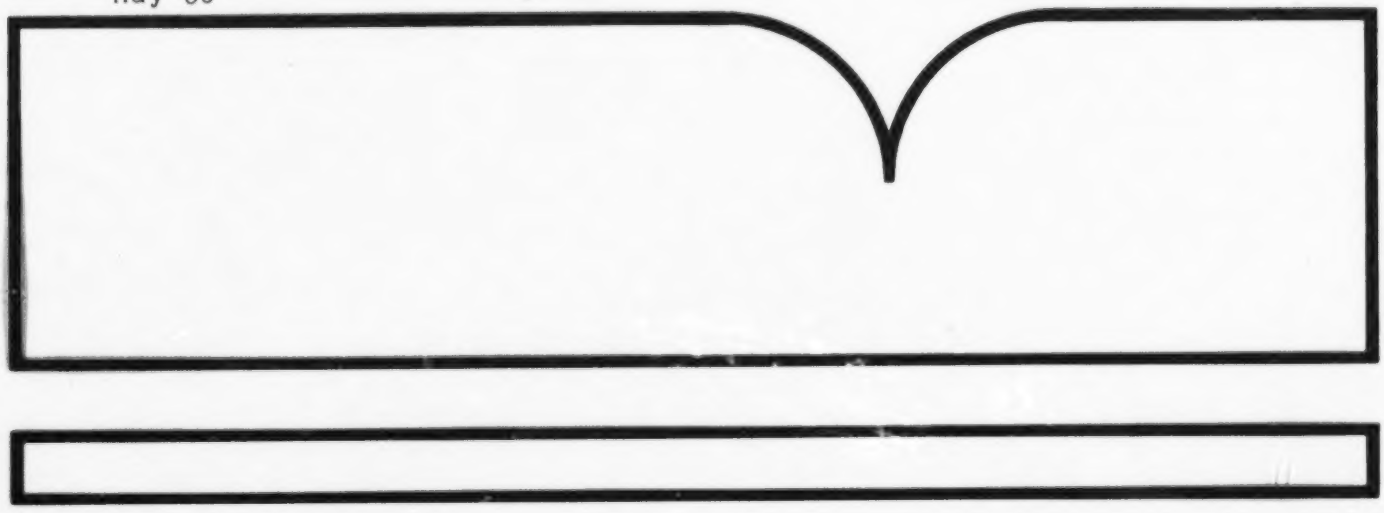

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LABORATORY TECHNIQUE FOR MEASUREMENT OF pH FOR CORROSION CONTROL STUDIES AND WATER NOT IN EQUILIBRIUM WITH THE ATMOSPHERE

By

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JAWWA, 72, 304-306 (May 1980)

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Municipal Environmental Research Laboratory
Office of Research and Development
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16. ABSTRACT

Factors governing pH changes that samples taken from systems closed to the atmosphere (pipe corrosion loops, distribution mains, household plumbing, ground and hypolimnotic waters) may undergo before and during conventional pH measurement is briefly discussed. Noticeable pH changes attributable to sample measurement while open to a different carbon dioxide partial pressure than in the source location were observed. A procedure and apparatus is outlined to minimize sample contact with the atmosphere during pH measurement, resulting in greater accuracy and reproducibility. Several other procedures to improve pH accuracy relating to electrode calibration and buffer solution storage are discussed.

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Laboratory Technique for Measurement of pH for Corrosion Control Studies and Water Not in Equilibrium With the Atmosphere

Michael R. Schock, William Mueller, and Ralph W. Buelow

Water quality analyses are very sensitive, and it is critical that the pH be measured as accurately as possible. This technique was developed after the authors observed that many water utility and research laboratory personnel follow poor techniques for determining pH.

The measurement and regulation of pH can be very critical in corrosion control in water distribution systems. At pH values below 8.4 a small difference in pH can account for a relatively large difference in calcium concentration or alkalinity when applied to a calcium carbonate saturation condition. For example, a water would be at calcium carbonate (as calcite) saturation at the following conditions: 15°C, 400 mg/L total dissolved solids (TDS), pH 8.0, alkalinity 120 mg/L (as $CaCO_3$), and a calcium concentration of 120 mg/L (as $CaCO_3$).[1] If the pH of this solution were decreased to 7.8, the calcium concentration required to retain $CaCO_3$ saturation would be 185 mg/L as $CaCO_3$, assuming the other water quality factors remained unchanged. In this case 0.2 pH units are equivalent to about 65 mg/L calcium as $CaCO_3$.

The solubilities of many other solids that could act as a control on the soluble levels of potentially toxic elements or that may provide pipe protection [such as $Pb_3(CO_3)_2(OH)_2$, amorphous $Fe(OH)_3$, or $Ca_5(PO_4)_3OH$] are also very pH dependent. These considerations and the cited case indicate the necessity to obtain maximum accuracy in pH measurement.

Influence of Atmospheric Carbon Dioxide

If the pH of a water sample is higher than the pH of its equilibrium state with the atmosphere, the observed pH will decrease if the sample is left open in the air while being measured. On the other hand, if the pH of a water sample is lower than its equilibrium state with the atmosphere, the pH will increase during measurement if precautions are not taken.[2-4] When using experimental systems that were sealed from exposure to the atmosphere, the pH has been found to differ by 0.3 to 0.7 units from data obtained by using a bench pH meter with the sample exposed to the atmosphere.

Table 1 illustrates the problem of measuring the pH of a water sample from a sealed system when the sample is exposed to the atmosphere. The conditions in the sealed system were pH 8.5, total alkalinity ~20 mg/L as $CaCO_3$, and room temperature.

The two meters used in this study agreed when operated under open conditions on the bench, but not when the electrode of one of them was installed in a sealed tank with internal circulation.

The variable readings were in part caused by the choice of the analyst as to when pH equilibrium was reached. This variability is eliminated by performing the pH measurement under sealed conditions.

Well waters, household plumbing lines, municipal distribution lines, and hypolimnetic lake waters often fall into the category of sealed systems. To demonstrate this problem, a well water sample was collected from a sealed system. Its pH was 4.7 when determined open to the atmosphere on a sample obtained in an unsealed container. To determine the effect of contact with the atmosphere, a second sample was collected in a sealed bottle. This time the pH was 4.1. The actual pH was possibly somewhat lower than 4.1, because the pH test was still performed open to the atmosphere.

Roberson et al[5] found that the difference between some field and laboratory pH measurements ranged from 0.0 to 2.8 pH units. In general, they observed the pH measurements to be higher in the field than in the laboratory. They attributed many of the pH increases and decreases to changes in CO_2 concentrations in the water.

Influence of Other Chemical Factors

Variations in the pH from the time of sampling to measurement in the laboratory can also be caused by precipitation and aging of particulate material in the container (such as $CaCO_3$ or ferric oxyhydroxide), organism growth and respiration, and, more rarely, reaction with the container itself. Care should be taken to disturb the natural state of the sample as little as possible by the sampling procedure itself, as even brief exposures to the air of samples from closed systems may induce irreversible redox reactions or other chemical changes that could alter the pH.

Recommended Procedure

Prior to using a pH meter for any analytical determination the meter should be calibrated by using standard buffer solutions. The calibration should include a range of pH values—for example, pH 4, pH 7, and pH 10—to determine how the meter and electrode respond to pH changes. A properly operating meter and electrode system will measure the range of standard buffers accurately within about ± 0.1 pH without recalibrating. The meter instructions manual

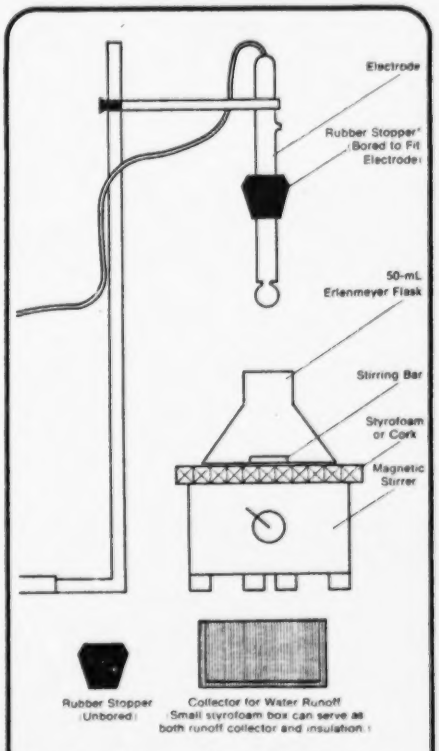
Electrode
Rubber Stopper* (Bored to Fit Electrode)
50-mL Erlenmeyer Flask
Stirring Bar
Styrofoam or Cork
Magnetic Stirrer
Rubber Stopper (Unbored)
Collector for Water Runoff (Small styrofoam box can serve as both runoff collector and insulation.)
*If a dual electrode system is used, a larger stopper will have to be bored to fit the electrodes and the selected sample container.

Fig. 1. Apparatus for Measuring pH

or a suitable reference[6] may be consulted for details on testing the electrical function of the system. At least two buffer standards should be used and should bracket the expected sample pH if possible. The buffers should be at or near the same temperature as the sample if using the temperature compensator on the meter is not possible. On many meters this device is used to correct for a non-ideal electrode slope,[6] and then cannot be used for subsequent temperature adjustment.

Experience in the authors' laboratory with many different designs of electrodes and meters has been that meter malfunctions are quite rare compared to those of electrodes. To detect poor electrode performance, it is a useful practice to have several sets of electrodes on hand and to compare readings taken on replicates of several samples of varying pH and alkalinity using different combinations of meters and electrodes. Even some new electrodes have occasionally worked improperly from their first use. Caution must be observed to allow for a breaking-in period of several hours to several days in some cases before fast, reproducible response is attained. Storage of electrodes between uses in a slightly acidic KCL solution has been found helpful.[6]

To avoid the inaccuracy in pH measurements caused by exposure to atmospheric CO_2, a simple pH-measuring technique that eliminated drifting and provided pH values using a laboratory bench meter essentially the same as those in a sealed system was devised. A description of the method, which is an elaboration and refinement of that contained in *Standard Methods*,[7] plus a sketch of the equipment follows.

The necessary apparatus is identified in Fig. 1. Figures 2 and 3 are photographs of single and dual electrode setups, respectively. Whenever pH measurements are made the stopper must contact the water surface. The dual electrode unit shown in Fig. 3 was being used for alkalinity titrations.

1. The pH meter must be warmed up and standardized. Buffers should not be stored open to the atmosphere between uses and should preferably be measured in the same closed configuration as the samples. Buffers and samples should be at the same temperature, or a reliable compensation method must be employed.[2,6-8] The meter should be turned to "standby."

2. The sample is collected in a 50-mL Erlenmeyer flask by filling it completely to the top allowing overflow of a half to an entire flask volume if the sample solution is plentiful. If possible, the sample solution should be introduced below the surface in the flask to minimize air contact.

3. The electrode is rinsed with distilled water from all sides, and the rinse is repeated. The electrode may be blotted dry with a soft tissue if extreme care is taken not to scratch the bulb or the junction. Blotting may slow the electrode response in some cases, however.

4. The solid stopper is taken out of the Erlenmeyer flask, the stirring bar is placed in the flask, and the electrode is placed in the flask so that the bored stopper seals it in place. Some water will be displaced during this step, and this should be caught in a runoff collector.

5. The flask should be placed on a styrofoam or cork pad (which serves as an insulator) on the magnetic stirrer. If a styrofoam runoff collector is used it can serve as insulation as well, and the pad is not needed. Suitable styrofoam collectors (such as the ones shown) can often be made from the packing material for various laboratory items. Though not common, stirrers that are driven by laboratory air lines connected via tubing are available, which generate no heat and are comparatively inexpensive.

6. The meter is switched from "standby" to "pH" and the magnetic stirrer is turned on so that uniform flow past the electrode is achieved. The setting on the mixer will depend entirely on the kind of stirrer used. The stirring rate should be as constant as possible from sample to sample, so a stirring apparatus with separate spin control and on-off switch is convenient. A high stirring velocity has been observed to raise the sample temperature through friction, draw in air from around the stopper, and increase the noise in the pH reading by affecting the junction potential of the electrode.[6] The extent to which these problems occur must be evaluated for each particular system by the user.

7. A stable reading should be reached in approximately 0.5 to 3 min with a properly functioning electrode, except in cases where successive samples are measured that have widely differing compositions, temperatures, or pH values.

8. The pH is read, the magnetic stirrer, is turned off, the meter is switched to "standby."

9. A new sample is started at step 2.

TABLE 1
Effect of Atmospheric Interaction on pH Measurement

Sample Number	pH Open to Air
1	8.20
2	7.80
3	8.28

Additional Precautions

Some, including the *Handbook for Analytical Quality Control*,[9] recommend that after rinsing the electrode with distilled water between samples, the electrode should be rinsed with or dipped several times in the new sample water before taking the pH measurement. In order to obtain a constant and accurate pH in samples with a low buffer capacity or when successive samples differ by

Fig. 2. Single Electrode Setup

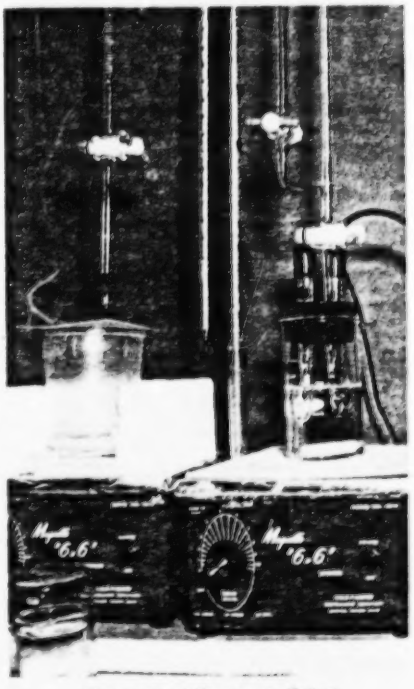

Fig. 3. Dual Electrode Setup

more than approximately 0.1 or 0.2 pH, replicate samples are advised. This requires repeating step 2 and steps 4 through 8 until a constant pH value is attained with successive portions of sample water. Several repetitions of this sequence may be required to obtain a constant and accurate value. The repetition serves to cleanse the electrode of any contamination or previous sample carryover, so the electrode should not be rinsed with distilled water between successive immersions in water from the same sample when using this procedure.

Screw-cap vials of 20 to 40 mL capacity with PTFE inserts have been found to be an excellent substitute for the 50-mL Erlenmeyer flasks, when used in conjunction with a combination electrode, small PTFE stirring bar, and the procedure outlined previously. When analyzing samples immediately in the field is not possible, these vials provide a sufficient seal against atmospheric interaction when filled leaving no airspace and closed tightly to maintain the pH for at least several days in many cases. The bottles should be inverted after closure and tightening to test for the presence of air bubbles that must be removed. Stable samples (no precipitation or redox reactions) with alkalinities of 50 to 150 mg/L as $CaCO_3$ and initial pH values of 7.5 to 8.9 have held their pH change to less than −0.05 units over three weeks in tests made in the authors' laboratory.

When pH measurements are to be used in the calculation of chemical equilibria, such as aqueous speciation and saturation states of solids, careful attention must be paid to the accuracy of the buffer solutions themselves. Commercially prepared solutions have been found on occasion to vary considerably from the values marked on the bottles, particularly with extended storage, even if unopened. Stability is a particular problem with buffers in the neutral to basic pH range made from phosphate, borate, or carbonate salts. These buffer compositions are especially sensitive to atmospheric CO_2. Some buffers are also subject to mold growth.[6]

Reference salts are available from the US National Bureau of Standards,[10] along with instructions for preparation of primary standard buffers of closely known pH. Buffers may also be prepared by using reagent salts in the proper ratios.[6-8] The stabilities of these solutions are from approximately four weeks to several months. For the greatest reliability, fresh solutions should be carefully prepared on about a monthly basis.[7,9] Figure 4 shows an apparatus that is useful for the storage of CO_2-sensitive reference buffer solutions.

pH is a function of temperature, and corrections should be made for changes resulting from measurement of a sample in a laboratory at a significantly different temperature than that of its actual environment at the time of sampling. The importance of such corrections depends upon the purpose of the study and the temperature range involved. An equation for making these corrections that is useful in many cases has been developed.[6]

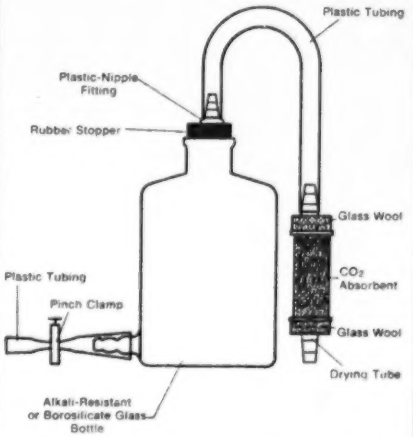

Fig. 4. Apparatus Used for Storage of CO_2-Sensitive Buffer Solutions

Joints may be covered with plastic film for further protection. Buffers of high pH may attack the glass after prolonged storage, altering the buffer pH value.

TABLE 2
*Stability of the Closed System Measuring Procedure Over 30 Min on a Very Low Alkalinity Sample**

Elapsed Time *min*	Open Beaker *pH*
1	8.12
5	7.98
10	7.79
20	7.55
30	7.39

*Closed system pH—8.16 ± 0.02 over 30 min. span; total alkalinity of source water—3.27 ± 0.01 mg/L as $CaCO_3$; temperature—25°C

Results

An example of the improved precision and accuracy attained using the described closed system measuring procedure is shown in Table 2. After cleansing the electrode three times, by following step 2 and steps 4 through 8 each time with the water to be analyzed, duplicate samples were measured from a closed experimental water tank with an analyzed total alkalinity of 3.27 ± 0.01 mg/L as $CaCO_3$ at 25°C. In both cases, over a 30-min time span the pH fluctuated by no more ± 0.02 units. Following the second 30-min measurement, a fresh sample was taken in an open 50-mL beaker, which was stirred at the same rate as the closed samples while the pH was monitored. After 30 min the observed pH had decreased by almost 0.8 units and was still decreasing at the end of the test.

Conclusions

1. Maintaining a sample under sealed conditions after collection and during pH measurement can eliminate meter drift caused by interaction with atmospheric CO_2.

2. This method is not suggested as being necessary in all cases. If the sample is already in equilibrium with the atmosphere or if it has a very high buffer capacity, it is not needed. Unless a sample is run both ways, however, no definite decision can be made on whether or not this technique would be useful in any particular case. In order to eliminate the need to check equilibrium, performing all pH measurements under sealed conditions might be easier if drifting problems are ever experienced.

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